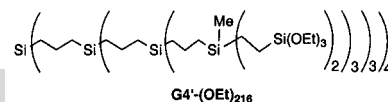


# Carbosilane Dendrimers as Nanoscopic Building Blocks for Hybrid Organic–Inorganic Materials and Catalyst Supports\*\*

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*Advanced nanoarchitectures can be achieved by covalent linking of dendrimeric modules into porous networks using sol–gel chemistry. The focus of this work lies in the conversion of second, third, and fourth generation carbosilane dendrimers to high surface area xerogels and aerogels, and the use of these materials as catalyst supports. By varying the hydrolysis solvent and dendrimeric precursor employed, the properties of the nanoarchitectures can be easily tuned. In particular, triethoxysilyl-terminated dendrimers have been hydrolyzed in solvents of varying polarity with acid catalysts to produce micro- and mesoporous hybrid dendrimer xerogels and aerogels with a controllable degree of Si–OH functionality.*

## 1. Introduction

Nanostructured materials with well-defined and tunable porosities have attracted considerable recent interest in chemistry and materials science, due to their potential applications in catalysis,<sup>[1]</sup> optical devices,<sup>[2]</sup> separations,<sup>[3]</sup> and microelectronics.<sup>[4]</sup> The construction of such materials represents a considerable synthetic challenge, which may be addressed with methodologies that feature nanoscopic molecular building blocks. For example, oligomeric surfactants are often employed to template the formation of nanoporous solids.<sup>[5]</sup> Another type of building block that has received significant interest is dendrimeric macromolecules.<sup>[6]</sup> In fact, these materials were proposed as modules for advanced nanoarchitectures some time ago.<sup>[7]</sup> We have been exploring the use of dendrimers in materials synthesis via two different strategies based on models for the close-packing of spherical objects. Thus, spherically shaped dendrimers should assemble into porous networks with porosities that are determined by the radius of the dendrimeric building block. One approach involves the combination of oppositely charged dendrimers possessing anionic or cationic endgroups.<sup>[8]</sup> A second strategy utilizes

condensation reactions which covalently link dendrimers into a three-dimensional network.<sup>[9,10]</sup> The latter approach is the subject of this report.

We have chosen to employ carbosilane dendrimers as building blocks, since they appear to be relatively rigid and approximately spherical in shape.<sup>[11]</sup> In the approach described here, these dendrimeric modules are covalently linked into porous networks using sol–gel chemistry. In particular, triethoxysilyl-terminated dendrimers have been hydrolyzed with acid catalysts to produce micro- and mesoporous hybrid dendrimer–silica xerogels and aerogels. The acidic conditions employed for these synthetic investigations promote the formation of Si–OH functionalities, which are of use in applications of the new materials as catalyst supports. Prior to our studies, there had been considerable research on the synthesis of hybrid organic–inorganic materials via sol–gel methods.<sup>[12–14]</sup> We have focused on the conversion of second, third, and fourth generation carbosilane dendrimers to high surface area xerogels and aerogels, and use of these materials as catalyst supports.<sup>[9,10,15]</sup>

## 2. Synthesis of Dendrimer-Based Xerogels and Aerogels

The carbosilane dendrimers were synthesized according to known methodologies, involving hydrosilation of terminal olefinic groups with  $\text{HSiCl}_3$ , followed by vinyl (or allyl) Grignard addition to the resulting trichlorosilyl functionalities.<sup>[16]</sup> In order to cap the dendrimers with  $(\text{RO})_3\text{Si-}$  groups, we employed the direct hydrosilation of vinyl-terminated species with triethoxysilane. A representative example of our syn-

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thetic scheme is shown in Figure 1, which illustrates conversion of a second-generation carbosilane dendrimer terminated by 36 allyl groups (G2-Al<sub>36</sub>) to the corresponding fourth-generation sol-gel precursor G4'-(OEt)<sub>216</sub>.

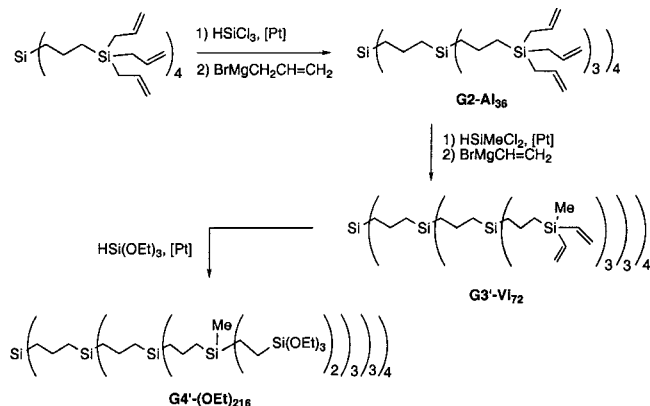


Fig. 1. Synthetic scheme for the synthesis of trialkoxysilyl-terminated carbosilane dendrimers.

Hydrolyses of G2-(OEt)<sub>36</sub> and G3-(OEt)<sub>108</sub> in tetrahydrofuran (THF) solutions in the presence of small quantities of 1 N HCl produced the xerogels X-G2<sub>THF</sub> and X-G3<sub>THF</sub>.<sup>[17]</sup> Surprisingly, the nitrogen porosimetry data (Table 1) indicate that there is an increase in the total surface area and pore volume with generation number. That is, as the diameter of the

The major cause of pore collapse during desiccation of a wet gel is the large capillary force derived from the (usually polar) solvent leaving the network structure. Thus, the use of a nonpolar solvent in sol-gel chemistry is highly desirable from the standpoint of minimizing pore collapse.<sup>[18]</sup> We attempted the hydrolyses of G2-(OEt)<sub>36</sub> and G3-(OEt)<sub>108</sub> in benzene solution with small quantities of 1 N HCl. After several days, the heterogeneous sol solutions gelled to yield hard, clear, homogeneous monoliths, from which the xerogels X-G2<sub>benz</sub> and X-G3<sub>benz</sub> were obtained. As shown in Table 1, these xerogels are mesoporous and display an increasing surface area with increasing dendrimer generation. Thus, the compressibility phenomenon of the condensed dendrimers observed in X-G2<sub>THF</sub> and X-G3<sub>THF</sub> is apparently still operative in X-G2<sub>benz</sub> and X-G3<sub>benz</sub>. Perhaps more significantly, compared to X-G2<sub>THF</sub> and X-G3<sub>THF</sub>, the surface areas of the xerogels made in benzene nearly doubled (see Table 1).

In an effort to obtain xerogels with even higher surface areas, the wet solid monoliths obtained from hydrolyses of G2-(OEt)<sub>36</sub> and G3-(OEt)<sub>108</sub> in benzene were heated at 100 °C for 48 h in toluene, and this gave X-G2<sub>HT</sub> and X-G3<sub>HT</sub> with extremely high surface areas (Table 1). The washing process probably aids in the removal of the polar species EtOH and H<sub>2</sub>O entrapped in the pore structure of the wet gels. Interestingly, the toluene washing induces a surface area trend that is now consistent with that expected for the packing of hard spheres (see Table 1).

It is significant to note that low molecular weight alkoxy-silanes did not gel under the same conditions employed for hydrolysis of the dendrimers. In fact, the hydrolysis of such species (e.g., Si(OEt)<sub>4</sub>, 4,4'-bis(triethoxysilyl)biphenyl, and G1-(OEt)<sub>12</sub>) typically yield precipitates with low surface areas. Thus, the formation of polymeric gels in the case of the second- and third-generation dendrimers may be associated with their highly hydrophobic interior, which (despite their hydrophilic periphery) keeps them dissolved in solution during the condensation process.

Another attempt to produce very high surface areas in the dendrimer-based gels involved supercritical CO<sub>2</sub> extraction of the monoliths obtained from hydrolysis of G2-(OEt)<sub>36</sub> and G3-(OEt)<sub>108</sub>.<sup>[15]</sup> This processing method provided the aerogels A-G2<sub>THF</sub>, A-G3<sub>THF</sub>, A-G2<sub>benz</sub>, and A-G3<sub>benz</sub>, which display surface areas and pore volumes that increase on going from the second- to the third-generation dendrimers (Table 1). Thus, the condensed dendrimers of A-G2<sub>THF</sub> and A-G2<sub>benz</sub> appear to be compressed on to one another more than those of A-G3<sub>THF</sub> and A-G3<sub>benz</sub>.

Dendrimer-based xerogels and aerogels were also synthesized from fourth generation alkoxy-silyl-terminated carbosilane dendrimers (G4'-(OEt)<sub>216</sub>). However, these precursors are not monodisperse and have a slightly different backbone than G2-(OEt)<sub>36</sub> and G3-(OEt)<sub>108</sub>, in that G4'-(OEt)<sub>216</sub> was synthesized by hydrosilation of the third generation -Si-Me(CH=CH<sub>2</sub>)<sub>2</sub>-terminated dendrimer (G3'-Vi<sub>72</sub>) with HSi(OEt)<sub>3</sub>. Therefore, direct comparisons with G2-(OEt)<sub>36</sub> and G3-(OEt)<sub>108</sub> are not possible. However, a qualitative

Table 1. Nitrogen porosimetry and <sup>29</sup>Si CP MAS NMR spectroscopic data for the xerogels and aerogels.

Xerogel or aerogel	Surface area [m <sup>2</sup> /g]	Pore volume [cc/g]	Pore radius [Å]	Micro-pore area [m <sup>2</sup> /g]	T <sup>1</sup> [%]	T <sup>2</sup> [%]	T <sup>3</sup> [%]	Degree of condensation [%]
X-G2 <sub>THF</sub>	325	0.21	13	225	5.6	83.8	10.6	68.3
X-G3 <sub>THF</sub>	490	0.33	14	270	5.0	85.9	9.1	68.0
X-G4 <sub>THF</sub>	30	0.04	10	20	—	—	—	—
X-G2 <sub>benz</sub>	615	0.36	15	165	8.2	67.3	24.6	72.1
X-G3 <sub>benz</sub>	805	0.70	17	100	8.6	68.5	22.9	71.4
X-G4 <sub>benz</sub>	445	0.28	12	70	—	—	—	—
X-G2 <sub>HT</sub>	1335	2.08	31	0	6.1	57.4	36.5	76.8
X-G3 <sub>HT</sub>	1005	0.96	19	45	6.8	74.6	18.6	70.6
X-G2 <sub>Ti</sub>	635	1.13	35	0	0	58.0	42.0	—
X-G3 <sub>Ti</sub>	485	0.53	22	47	0	26.6	73.4	—
X-G2 <sub>Ti/Si</sub>	765	1.18	31	101	0	54.0	46.0	—
A-G2 <sub>THF</sub>	880	1.81	39	144	60	—	—	—
A-G3 <sub>THF</sub>	950	2.00	42	148	35	—	—	—
A-G2 <sub>benz</sub>	800	1.86	47	219	0	—	—	—
A-G3 <sub>benz</sub>	950	2.59	55	155	20	—	—	—
A-G4 <sub>benz</sub>	700	1.44	42	10	25	—	—	—

dendrimeric building block increases, there is a concomitant increase in the surface area and pore volume of the corresponding gel. This observation is perhaps unexpected when one considers that, in the condensation of silica particles in the sol-gel process, the surface area of silica spheres generally decreases with increasing sphere size. We have explained this apparent anomaly by suggesting that G2-(OEt)<sub>36</sub> and G3-(OEt)<sub>108</sub> exhibit some degree of compressibility,<sup>[9,10]</sup> and that G2-(OEt)<sub>36</sub> is more compressible than G3-(OEt)<sub>108</sub> due to the less congested surface of the lower generation.

comparison of the porosimetry data for the second, third, and fourth generation dendrimer-based xerogels and aerogels reveals that all the G3 gels exhibit a maximum in both surface area and pore volume (Table 1). This may suggest that G4'-(OEt)<sub>216</sub> is more rigid than the lower-generation dendrimers, and demonstrates sol-gel behavior that is more consistent with the condensation of silica particles.

### 3. Spectroscopic Properties of Dendrimer-Based Gels

Solid state <sup>29</sup>Si cross polarization magic angle spinning (CP MAS) nuclear magnetic resonance (NMR) spectroscopy was employed to determine the degree of condensation in the gels. The silicon centers in the condensed dendrimers are designated T<sup>1</sup>, T<sup>2</sup>, and T<sup>3</sup> to denote the presence of one, two, or three Si-O-Si linkages, respectively.<sup>[12]</sup> By deconvolution of the individual T<sub>n</sub> resonances, an estimate (±10 %) of the degree of condensation in the gels was made. Xerogels X-G2<sub>benz</sub> and X-G3<sub>benz</sub> have higher degrees of condensation than the corresponding xerogels produced in THF. Furthermore, there are more fully condensed silicon centers (T<sup>3</sup>) in the xerogels made in benzene. This is somewhat surprising due to the relative solubilities of H<sub>2</sub>O in THF and benzene, but suggests that the polymerizing dendrimeric species remain soluble in benzene solution, thereby allowing a high degree of condensation. It is also interesting to note that the <sup>29</sup>Si CP MAS NMR data for X-G2<sub>HT</sub> indicate that there has been further condensation during processing of the wet gel (Table 1). In particular, comparison of the T<sup>3</sup> values for X-G2<sub>benz</sub> and X-G2<sub>HT</sub> reveals a nearly 12 % increase in the number of fully condensed silicon centers upon high-temperature solvent processing. Since X-G2<sub>HT</sub> and X-G3<sub>HT</sub> were solvent-processed after gellation, it appears that subsequent condensations are occurring during this procedure. The gels treated with hot toluene have a high degree of site-isolated hydroxy groups (Table 1), which is useful in applications of these materials as catalyst supports.

### 4. Dendrimer-Based Materials as Catalyst Supports

While dendrimeric macromolecules have been used previously as homogeneous catalysts,<sup>[19]</sup> our materials present the opportunity to use dendrimers as key building blocks in heterogeneous catalysis. Further, the fact that these dendrimer-based gels possess high surface areas and a high content of Si-OH groups (e.g., X-G2<sub>HT</sub> has a surface hydroxyl coverage of 3.0 OH/nm<sup>2</sup>) suggests their use as catalyst supports. For comparison, typical surface hydroxyl coverages are 5.0–5.7 OH/nm<sup>2</sup> for silica aerogels, and 1.2–2.6 OH/nm<sup>2</sup> for partially dehydroxylated silicas.<sup>[18,20]</sup> Given our interest in the synthesis and study of site-isolated titanium catalysts for olefin epoxidation,<sup>[21]</sup> we sought to compare the properties of the dendrimer-based xerogels with silica as a catalyst support.

The xerogels X-G2<sub>HT</sub> and X-G3<sub>HT</sub> were treated with Ti(O<sup>i</sup>Pr)<sub>4</sub> to yield X-G2<sub>Ti</sub> and X-G3<sub>Ti</sub>, and X-G2<sub>HT</sub> was treated with the highly active epoxidation catalyst Ti[OSi(O<sup>i</sup>Bu)<sub>3</sub>]<sub>4</sub><sup>[21]</sup> to yield X-G2<sub>Ti/Si</sub>. These catalytic materials were employed in the epoxidation of cyclohexene. As shown in Figure 2, these catalysts produced moderate to high yields of cyclohexene oxide, especially relative to those for the well-known Shell catalyst. Interestingly, all three

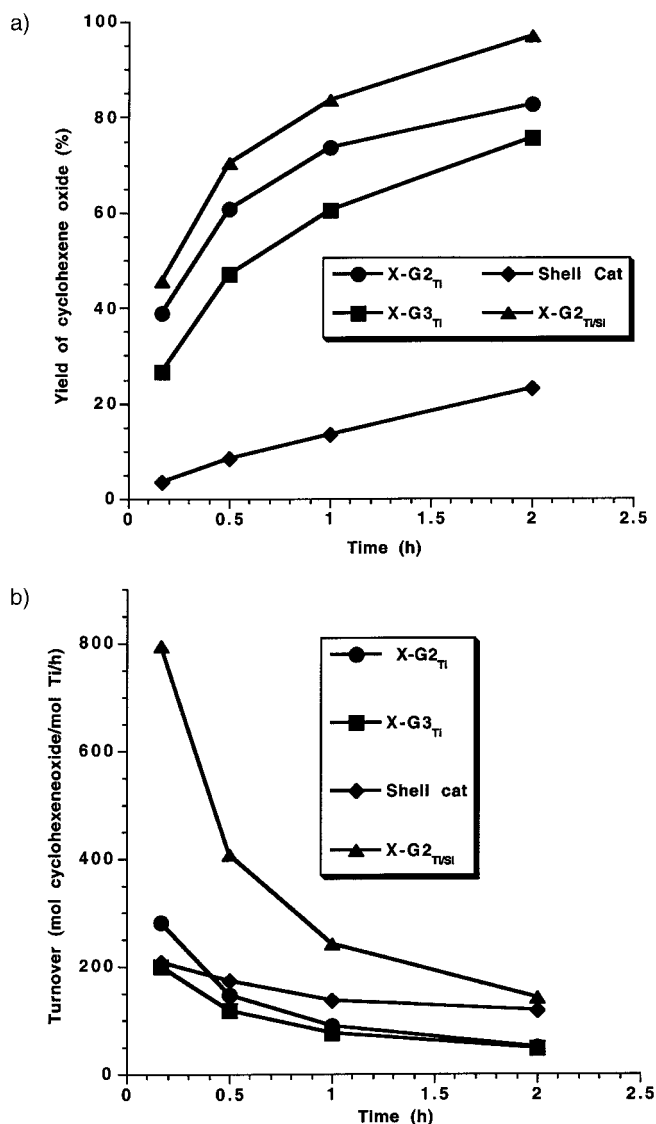


Fig. 2. Data for the catalytic epoxidation of cyclohexene with cumene hydroperoxide. a) Yield of cyclohexene oxide with time. b) Turnover frequencies as a function of time.

materials displayed a selectivity of 100 % over the 2 h reaction time. Moreover, Ti[OSi(O<sup>i</sup>Bu)<sub>3</sub>]<sub>4</sub> supported on X-G2<sub>HT</sub> (X-G2<sub>Ti/Si</sub>) is remarkably active, both in terms of cyclohexene oxide yield and turnover frequency. We propose that the alkoxy(siloxy) ligand environment of Ti[OSi(O<sup>i</sup>Bu)<sub>3</sub>]<sub>4</sub> facilitates the introduction of single-site -O-Ti(O-SiO<sub>3</sub>)

centers, which are thought to be most active in epoxidation catalysis.<sup>[21]</sup>

Given the high yields obtained from the epoxidation of cyclohexene with X-G2<sub>Ti/Si</sub>, the G2 and G3 aerogel materials were treated with excess Ti[OSi(O<sup>i</sup>Bu)<sub>3</sub>]<sub>4</sub> following a similar synthetic protocol for the Ti-grafting previously reported.<sup>[10]</sup> The aerogels were then tested for their catalytic activity using cyclohexene and cumene hydroperoxide as the oxidant over a 2 h catalytic run. Although the Ti-grafted aerogels exhibited 100 % selectivity, the yields were low compared to those obtained with X-G2<sub>Ti/Si</sub>. However, the grafted aerogel exhibiting the highest yield of cyclohexene oxide was derived from A-G3<sub>benz</sub>, which has the highest surface area and lowest surface hydroxyl coverage of all four aerogels. Thus, it seems that the most ideal supports are those that contain a high surface area and a relatively low surface hydroxyl coverage (to provide site-isolated titanium centers).

## 5. Conclusion

The studies described herein detail some of our recent work dendrimeric building blocks in sol-gel chemistry. Future work in this area will involve the use of a wider variety of dendrimeric shapes, sizes and flexibilities, and investigations of the resulting materials as catalyst supports.

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